

To:

NASA
Lewis Research Center
Auxiliary Power Generation Office
21000 Brookpark Road
Cleveland 35, Ohio
ATT: Mr. Daniel G. Soltis

② SECOND MONTHLY REPORT,

Covering Period 1 - 31 August, 1963,

for

Research & Development of a High
Capacity Nonaqueous Secondary Battery,

(N.A.S.A.) Contract Number NAS3 - 2780

(14-00000-2-200000)

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Submitted by:

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CURRENT STATUS OF PROGRAM

During August we have concentrated on two areas of study--the anodic behavior of zinc, mercury, and silver in selected aqueous media, and the synthesis of beryllium di-alkyls. The results of our efforts thus far are briefly described below. A more detailed presentation of our program will appear in the quarterly report.

Anodic Behavior of Zinc, Mercury, and Silver

The anodic behavior of zinc in alkaline media has been studied, varying the hydroxide and zincate ion concentrations. Our purpose has been primarily to develop convenient electrometric techniques for studying three important aspects of the behavior of zinc electrodes in alkaline solution. We consider the work done with zinc to be representative of the type of studies involved in the study of any metal electrode thermodynamically unstable in contact with an electrolyte.

We have first been concerned with the rate at which zinc reacts directly with solvent. This rate may be measured conveniently by following the increasing concentration of soluble zinc species chronopotentiometrically. Our experiments have not been sufficiently elaborate to measure the rate as accurately as is possible by this technique, but we have established that the reaction is sufficiently slow not to interfere with the other electrometric measurements.

Secondly, we have been concerned whether, on anodization, zinc is directly oxidized to an insoluble oxide or hydroxide which then dissolves or whether it is oxidized to a soluble species which, if the reaction layer is sufficiently saturated in appropriate species, may precipitate. Our measurements indicate that the latter is the case, since there is no evidence of significant film formation until the solution is saturated in zincate ion.

Finally we are concerned whether the slow rate of reactivity of zinc with electrolyte is due to the chemical formation of a passivating film, and if so get some measure of the amount of film so formed. Our measurements indicate that the amount of film formed is, in fact, negligible, being less than one molecular layer thick, and in fact is not unambiguously identifiable as an oxide or hydroxide film.

Our studies on the anodization of mercury have been performed with the objective of establishing general patterns of anodic behavior with particular regard for the relevance of these types of behavior to battery technology. We have focused on mercury for experimental convenience, and have studied its anodic behavior in chloride, bromide, hydroxide, thiocyanate, acetate, ammonia, and molybdate media.

In general, anodic films may vary from thick, porous films, highly permeable to ionic transport to thin, impermeable films. When a metal is anodized at constant current in a precipitating environment and the variation of potential with time is observed, an abrupt rise in potential normally occurs at some time, t , the "transition time." In general, for film formation, the empirical equation, $it^m = K$, expresses the relationship between current, i , and the transition time. The constants m and K reflect the properties of the film itself and the degree of inhibition the film offers to ionic movement. The relevance of this information to battery technology is clear, since in producing a high energy density cathode, the control necessitated in satisfying the prerequisite of highly efficient oxidation of the metal to the cathode salt demands a thorough knowledge of the properties of this salt film--these properties most conveniently expressed by the empirical parameters m and K .

Fortunately the anodic behavior of mercury varies sufficiently from one environment to another as to make this an excellent prototype system for the general study of such phenomena. Two extreme types of behavior have been encountered, that observed in chloride solutions and that observed in hydroxide media, Up to concentrations of hydroxide as high as 0.05 M. we find

that the values of m and K are such as to indicate that the formation of oxide film is limited only by the rate of diffusion of hydroxide ions, and that this diffusion is not impeded by the film itself. This is not true in chloride (and bromide) solutions, where, at concentrations of precipitant anion above 0.01 M, the effect of the film in impeding further oxidation is marked and at concentrations above 0.02 M the amount of film formed at given current is nearly independent of the concentration of chloride or bromide in solution.

We wish to emphasize that our work has differed from that of most other investigators in the field by our emphasis on low concentrations of precipitant anions, and on the variation in behavior with concentration. We feel this type of program is especially pertinent to work in non-aqueous solvents where maximum concentrations of ionic species are relatively low.

Experiments in the other media listed above have been complicated by the complex equilibria extant in the reaction layer (the region of solution next to the electrode wherein the electrolyte composition differs from that in the bulk solution by virtue of changes induced by the passage of anodic current). It is clear that anodization behavior cannot be simply predicted from a knowledge of the appropriate equilibrium constants; for example, bromide and thiocyanate solutions which should behave similarly on mercury anodization in fact differ markedly. The effect of very small concentrations of mercury (II) is also quite pronounced. Whether this arises from nucleation phenomena or through its role in the complex equilibria prevailing in the reaction layer is not yet clear.

The anodic behavior of silver has been studied in aqueous chloride media. Our results indicate that the current-transition time relationship is given by $it^{0.5} = kC_{Cl^-}$, indicating the process to be limited by the diffusion of chloride ions, and that the film is perfectly permeable to ionic migration. We are now beginning work on the anodization behavior of silver in acetone-chloride media.

Synthesis of Beryllium Di-alkyl Compounds

During August we have begun work on the synthesis of beryllium di-alkyl compounds. It is then our intention to combine these with alkali halides. Complex salts of the form $\text{MX} \cdot 2\text{BeR}_2$ are reported to form which are liquid at room or slightly elevated temperatures and have the electrical properties of fused salts. The value of such materials in a non-aqueous cell is obvious.

Thus far, we have successfully synthesized di-methyl beryllium and are currently analyzing the product. Experimental difficulties result from the extreme sensitivity of the reaction intermediates and the product to oxygen and water, and the hazards attendant on work with beryllium.

WORK PROJECTED FOR SEPTEMBER

During September we expect to complete our study of the polarization behavior of the silver-silver chloride electrode in acetone. We are particularly interested in observing any differences in behavior which can be ascribed to the use of a non-aqueous solvent, and in determining the degree to which techniques of measurement applicable to aqueous systems can be directly applied to the more poorly conducting non-aqueous systems and the modifications which may be necessitated. Work on the anodization behavior of mercury will continue, and we shall shortly begin studies in appropriate non-aqueous solvents.

We shall continue work on the synthesis of beryllium di-alkyls and hope, by the end of September, to have a sufficiently clear idea of the physical and electrical properties of these materials and their derivatives to be able to determine the usefulness of pursuing this area further.

Manpower and Dollar Expenditures During

Period 1 - 31 August 1963 on

Contract No. NAS3-2780

Manhours

Dr. K. R. Hill	168 hours
Dr. R. G. Selim	160 hours
Dr. T. C. Wilder	160 hours
D. G. Conning	120 hours
G. Boyle	160 hours
R. Holmes	120 hours

Materials:

8/14/63	Dow-Corning		\$ 4.80
8/14/63	Penn-Chem Corp		83.08
8/14/63	Henry Troemner		99.30
8/27/63	Fisher	P.O. #4584	28.80
8/30/63	Fisher	P.O. #4635	205.12
8/26/63	Fisher	P.O. #4563	426.38

Note: Manhours and material costs are only approximations. Accurate figures will be submitted by the Corporate Accounting Department at the end of the monthly accounting period.